



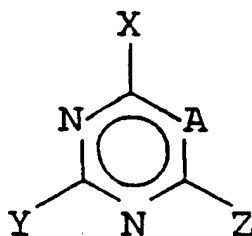
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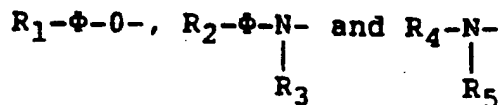
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(54) Title: SUBSTITUTED PYRIMIDINES AND SUBSTITUTED TRIAZINES AS RUBBER-TO-METAL ADHESION PROMOTERS



(I)



(II)

(57) Abstract

This invention relates to the improvement of rubber-to-metal adhesion and adhesion retention in sulfur vulcanizable, metal reinforced rubber compositions via the use of substituted pyrimidine and triazine adhesion promoters of structure (I), wherein A is N or C-H, X, Y and Z are independently selected from the group consisting of chloro, (II) wherein R<sub>1</sub> may be hydrogen, chloro, acyl, or C<sub>1</sub>-C<sub>12</sub> alkyl; R<sub>2</sub> may be hydrogen, C<sub>1</sub>-C<sub>12</sub> alkyl, chloro, hydroxy, alkoxy, or anilino; R<sub>3</sub> may be hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl; R<sub>4</sub> may be hydrogen, C<sub>1</sub>-C<sub>8</sub> alkyl, cyclohexyl, C<sub>1</sub>-C<sub>12</sub> hydroxyalkyl, or C<sub>1</sub>-C<sub>12</sub> alkoxyalkyl; R<sub>5</sub> may be hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, cyclohexyl, or C<sub>1</sub>-C<sub>12</sub> hydroxyalkyl; with the proviso that Z may not be chloro when both X and Y are chloro.

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SUBSTITUTED PYRIMIDINES AND SUBSTITUTED TRIAZINES AS  
RUBBER-TO-METAL ADHESION PROMOTERS

TECHNICAL FIELD

10       The present invention is directed toward improving the adhesion and adhesion retention between rubber compositions, such as those used in the manufacture of tires, conveyor belts, hoses and the like and brass coated wire or cable which is embedded in the stock.

15       The improved useful life of modern rubber compositions, especially in belting and tire end uses via more sophisticated and effective antiozonant/antioxidant packages have necessitated the desirability of adding materials to the rubber compositions to improve useful  
20       article life and service through increased reinforcing agent adhesion and adhesion retention. Improved adhesion between rubber and brass coated wire is obtained according to the present invention.

BACKGROUND ART

25       It is often desirable to reinforce rubber articles by incorporating therein metal reinforcing elements. For example, tires, conveyor belts, power transmission belts, timing belts, hoses and a variety of other rubber articles are often reinforced with metal wire. In order  
30       for rubber articles which are provided with steel

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reinforcing elements to function effectively, it is important that good adhesion between the rubber and the metal reinforcing elements be maintained. One of the most common methods of enhancing the adhesion of wire filaments to rubber is to coat the filament with another material, for example, pneumatic vehicle tires are often reinforced with cords prepared from steel filaments which are coated with brass. Normally, steel reinforcing elements are coated with a brass that is an alloy of copper and zinc.

It is also known that various agents can be mixed into the rubber which will increase adhesion between the rubber and metal reinforcements embedded in it. U.S. Patent No. 3,894,903 discloses a process for improving the bonding of rubber to copper and copper alloys by incorporating into the rubber before vulcanization certain triazines, for example 2-(3-hydroxyphenoxy)-4-chloro-6-aminotriazine.

Peroxide initiated curing systems for rubbery materials have proven to be unsatisfactory in the production of finished articles that are required to have extended flex life, for peroxide cured rubbers tend to crack when subject to repeated flexing. Additionally, peroxide curing systems tend to be expensive and because of their reactivity, they require careful handling to avoid the creation of a dangerous environment.

As a result, many industries, such as the tire and industrial belting industries prefer to use sulfur cure vulcanization systems for cross-linking rubber.

### SUMMARY OF THE INVENTION

This invention reveals the use of substituted triazines and substituted pyrimidines in sulfur curable rubber-metal composites to increase the adhesion and adhesion retention between the metal and the rubber composition. Furthermore, most of the adhesion promoters of this invention do not negatively affect the processing or cured properties of the systems as is often the case with previous adhesion promoters. As a result of the retention of the inherently desirable properties of the system, the composites are useful in finished goods requiring long life, such as tires or industrial belting.

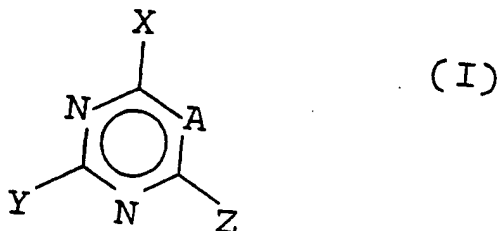
More specifically, this invention discloses a composite comprising a sulfur curable rubber composition with brass coated metal wire embedded therein wherein said rubber composition contains from about 0.05 to about 20 parts per hundred parts of rubber of at least one adhesion promoter selected from substituted triazines or pyrimidines according to Structure (I) below.

### DETAILED DESCRIPTION OF THE INVENTION

This invention relates to sulfur curable rubber compositions reinforced with brass coated metal wherein the composition contains certain substituted pyrimidine and substituted triazine adhesion promoters and composite articles made therefrom.

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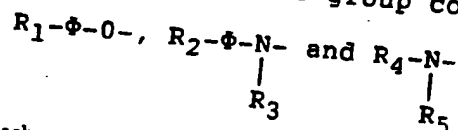
The compounds useful as adhesion promoters are those represented by structural formula (I) below:



5

wherein A is N or C-H, X, Y and Z are independently selected from the group consisting of chloro,

10



wherein  $R_1$  is hydrogen, chloro, acyl, or  $C_1-C_{12}$  alkyl;

$R_2$  may be hydrogen,  $C_1-C_{12}$  alkyl, chloro, hydroxy, alkoxy, or anilino;

15

$R_3$  may be hydrogen,  $C_1-C_4$  alkyl or phenyl;

$R_4$  may be hydrogen,  $C_1-C_8$  alkyl, cyclohexyl,  $C_1-C_{12}$  hydroxyalkyl, or  $C_1-C_{12}$  alkoxyalkyl;

$R_5$  may be hydrogen,  $C_1-C_4$  alkyl, cyclohexyl, or  $C_1-C_{12}$  hydroxyalkyl; with the proviso that Z may not

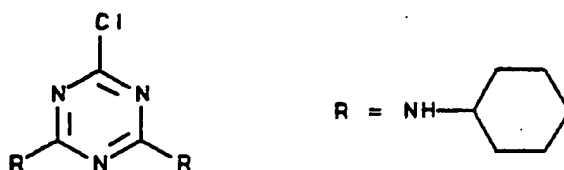
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be chloro when both X and Y are chloro and  $R_2$  may not be anilino when X, Y or Z is chloro.

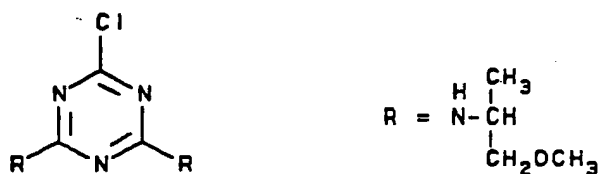
The following compounds represent preferred compounds of Structure (I) exhibiting good wire adhesion results.

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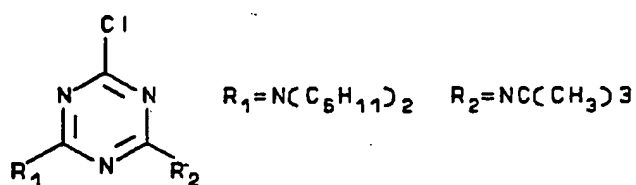
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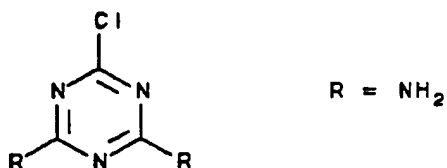
EX. 2 2-chloro-4,6-bis-(N-1-methoxy-2-propylamino)-1,3,5-triazine



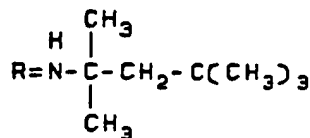
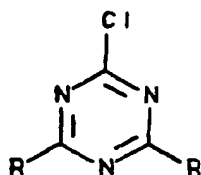
EX. 3 2-chloro-4-(N-tert-butylamino)-6-(N,N-dicyclohexylamino)-1,3,5-triazine



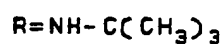
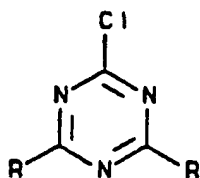
EX. 4 2,4-diamino-6-chloro-1,3,5-triazine



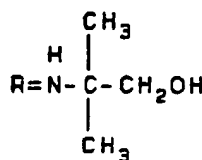
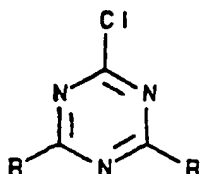
EX. 5 2-chloro-4,6-bis-(N-tert-octylamino)-1,3,5-triazine



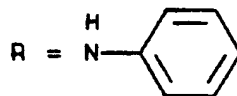
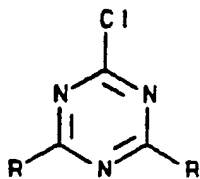
EX. 6 2-chloro-4,6-bis-(N-tert-butylamino)-1,3,5-triazine



EX. 7 2-chloro-4,6-bis-(N-2-methyl-1-propanolamino)-1,3,5-triazine

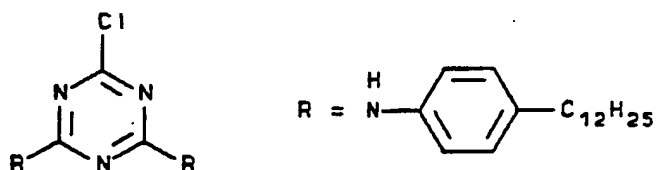


EX. 8 2-chloro-4,6-bis-(anilino)-1,3,5-triazine

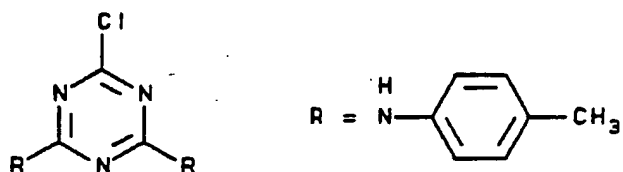




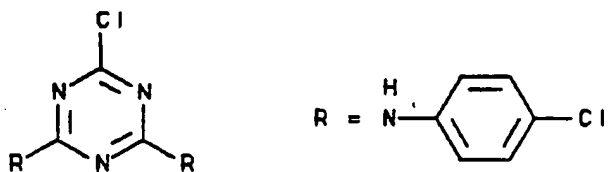
EX. 9 2-chloro-4,6-bis-(4-dodecylanilino)-1,3,5-triazine



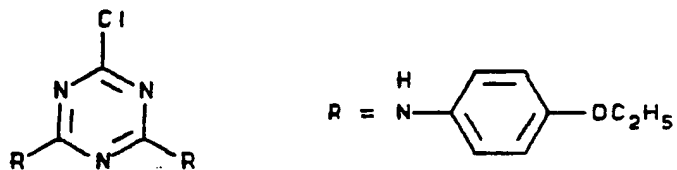
EX. 10 2-chloro-4,6-bis-(N-p-toluidine)-1,3,5-triazine



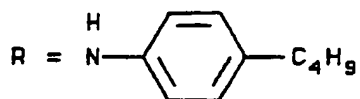
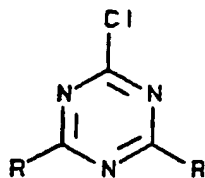
EX. 11 2-chloro-4,6-di-(4-chloranilino)-1,3,5-triazine



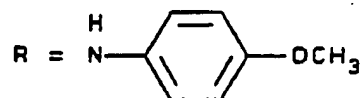
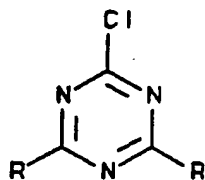
EX. 12 2-chloro-4,6-bis-(N-p-phenetidine)-1,3,5-triazine



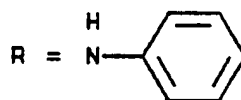
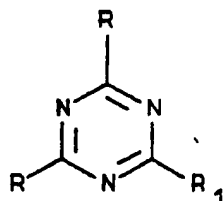
EX. 13 2-chloro-4,6-bis-(4-n-butylanilino)-1,3,5-triazine



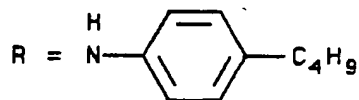
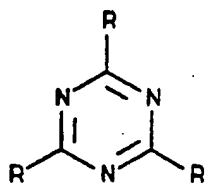
EX. 14 2-chloro-4,6-bis-(N-p-anisidino)-1,3,5-triazine



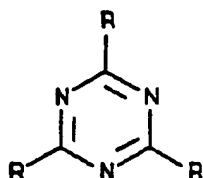
EX. 15 2,4,6-tris-(anilino)-1,3,5-triazine



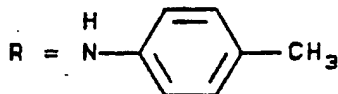
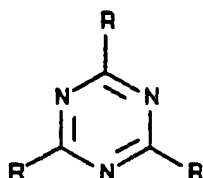
EX. 16 2,4,6-tris-(4-n-butylanilino)-1,3,5-triazine



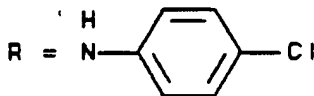
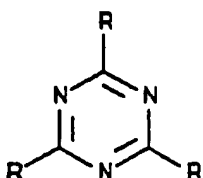
EX. 17 2,4,6-tris-(4-dodecylanilino)-1,3,5-triazine



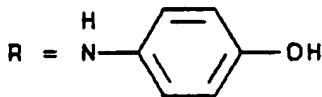
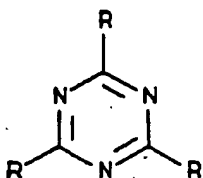
EX. 18 2,4,6-tris-(N-p-toluidine)-1,3,5-triazine



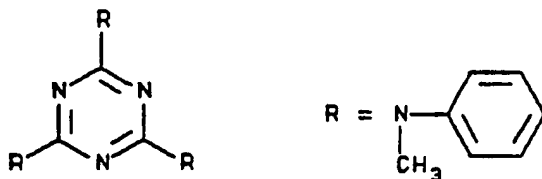
EX. 19 2,4,6-tris-(4-chloranilino)-1,3,5-triazine



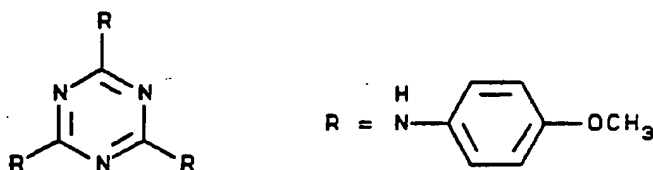
EX. 20 2,4,6-tris-(hydroxyanilino)-1,3,5-triazine



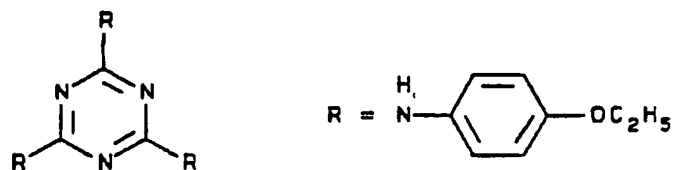
EX. 21 2,4,6-tris-(N-methyl-N-phenylamino)-1,3,5-triazine



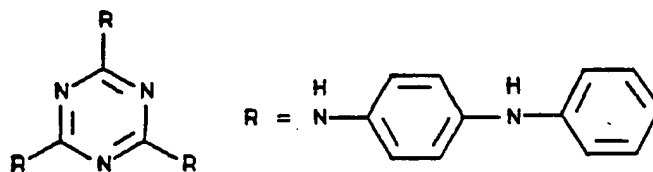
EX. 22 2,4,6-tris-(N-p-anisidino)-1,3,5-triazine



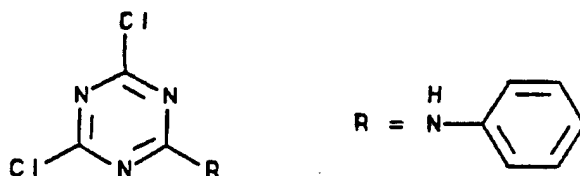
EX. 23 2,4,6-tris-(N-p-phenetidino)-1,3,5-triazine



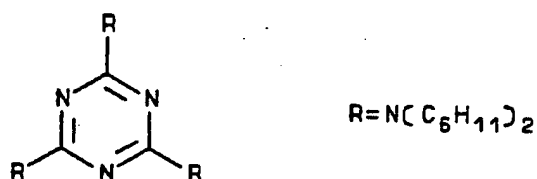
EX. 24 2,4,6-tris-(N-phenyl-p-phenylenediamino)-1,3,5-triazine



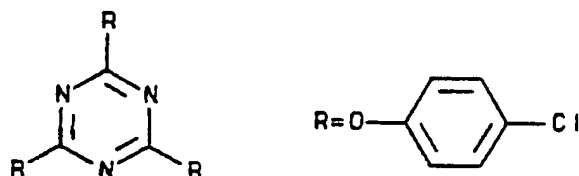
EX. 25 2,4-chloro-6-(anilino)-1,3,5-triazine



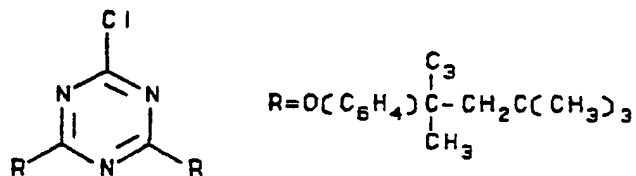
EX. 26 2,4,6-tris-(N,N-dicyclohexylamino)-1,3,5-triazine



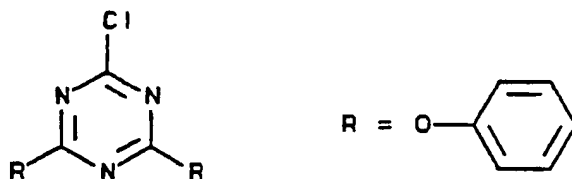
EX. 27 2,4,6-tris-4-chlorophenoxy-1,3,5-triazine



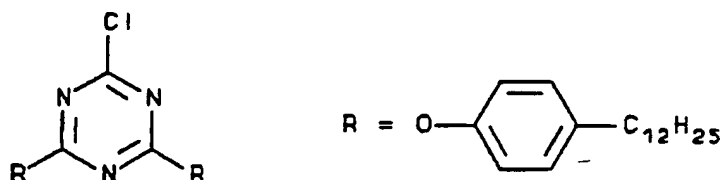
EX. 28 2-chloro-4,6-di-(4-tert-octylphenoxy)-1,3,5-triazine



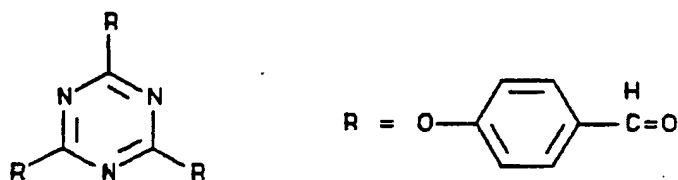
EX. 29 2-chloro-4,6-diphenoxy-1,3,5-triazine



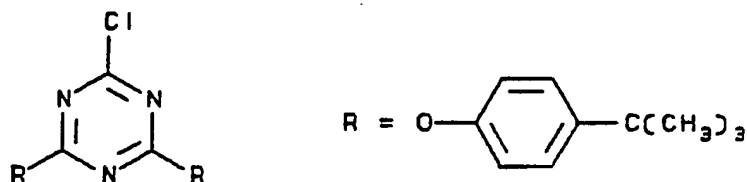
EX. 30 2-chloro-4,6-di-4-dodecylphenoxy-1,3,5-triazine



EX. 31 2,4,6-tris-(4-formylphenoxy)-1,3,5-triazine



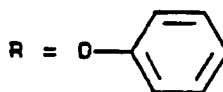
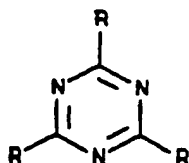
EX. 32 2-chloro-4,6-di-(4-tert-butylphenoxy)-1,3,5-triazine



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## EX. 33 2,4,6-triphenoxy-1,3,5-triazine

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The rubber in the composites of this invention can be selected from a wide variety of rubbery polymers for the instant adhesion promoters are effective in both natural and synthetic rubbers that are sulfur curable.

Some representative examples of rubbers commonly used in the composites of this invention include unsaturated elastomers such as natural rubber, styrene-butadiene rubber, synthetic polyisoprene, polychloroprene, cyclene rubbers, polybutadiene, nitrile rubbers, carboxylated nitrile rubbers, butyl rubbers, EPDM (ethylene-propylene-diene) rubbers, epichlorohydrin homo and copolymers, EPR (ethylene-propylene) rubbers, polyisobutylene, norbornene rubbers, polysulfide rubbers, and blends of various combinations of these and other diene rubbers.

The curative systems employed in the cross-linking of the compositions of this invention comprise sulfur and/or a sulfur donor compound and preferably, at least one sulfur cure accelerator.

The sulfur donor compounds which may be employed in conjunction with or in the alternative to sulfur are well known to those skilled in the art of rubber

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compounding. Illustrative of such sulfur donor compounds are 2-(4-morpholinodithio)benzothiazole, 4,4-dithio-dimorpholine, N,N'-caprolactam disulfide and the like.

5       The sulfur cure accelerators which may be employed include thioureas, such as N,N'-dibutylthiourea, 2-mercaptoimidazoline, tetramethylthiourea and the like; guanidine derivatives, such as N,N'-diphenylguanidine and the like; heterocyclics, such as mercaptobenzimi-  
10       dazole, mercaptobenzothiazole, 2,2'-dibenzothiazyl disulfide, zinc 2-mercaptobenzothiazole and the like; and sulfenamides, such as N-oxydiethylene-2-benzothiazolesulfenamide, N-t-butylbenzothiazolesulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N,N-diisopro-  
15       pyl-2-benzothiazolesulfenamide and the like. Moreover, mixtures of two or more sulfur cure accelerators may be employed in the curing agent of this invention. The preferred accelerators are thiazoles and sulfenamides, with sulfenamides being particularly preferred.

20       The sulfur cure accelerator is generally present in amounts of between about 0.1 parts and about 5 parts per 100 parts of rubber, with preferably between about 0.3 part and about 3.0 parts of accelerator per 100 parts of rubber being present. Most preferably, between about  
25       0.3 parts and about 2.0 parts of accelerator per 100 parts of rubber are employed.

Generally, between about 0.2 and about 10, preferably between about 3.0 and about 8.0 parts of sulfur per hundred parts of rubber are employed.



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Many terms are used to describe the metal reinforcing elements used to strengthen rubber articles. The terms "cord", "tire cord", "cable", "strand", "wire", "rod", "plate", and "filament" can all be used to describe metal reinforcing elements used to strengthen rubber articles. The term "metal reinforcement" as used herein is devised to be generic to all articles for reinforcing rubber articles including those listed above. Thus, without being limited thereto, a metal reinforcement can be a metal wire, metal cord, a metal tire cord, a metal cable, a metal strand, a metal rod, a metal plate or a metal filament.

The metal reinforcement elements which are generally preferred for use in this invention are brass plated steel.

Metal wires used in the tire industry are manufactured by cold drawing high carbon steel and subsequently brass plating same. The brass plating not only enhances the adhesion of the wire cord to rubber but also facilitates drawing the wire to a fine diameter of about 0.20 mm. The wire filaments are combined to form a strand and several strands combined to obtain the final tire cord.

The adhesion promoters of this invention are the tri-substituted pyrimidines and tri-substituted triazines Structure (I). Preferred are the triazines either alone or in combination with various commercially available bonding agents such as the cobalt salts, e.g.,

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cobalt stearate which is widely used in the tire industry; 2,3,5,6- tetrachloro-1,4-benzoquinone (sold by Uniroyal Chemical under the trademark VULKLOR); and various resorcinol/formaldehyde donors and resorcinol derivatives well known to the art. These systems are discussed in Encyclopedia of Chemical Technology ,vol. 20, pp. 365-468, 3rd edition (1982) and S. Buchan "Rubber to Metal Bonding", Crosby Lockwood and Sons London 1959 both of which are incorporated by reference.

10       The adhesion promoters of this invention can be mixed into a rubber using ordinary compounding techniques. Generally, it will be convenient to mix the adhesion promoter into the rubber composition of this invention simultaneously with other desired compounding ingredients using any suitable mixing equipment known to those skilled in the art, such as an internal mixer or mill. Normally, the rubber compositions used in the composites of this invention will be compounded with sulfur and carbon black. Numerous mineral fillers, such as clay and silica are commonly used as partial or total replacements for carbon black. The rubber compositions of this invention will also commonly contain cure accelerators, scorch inhibitors, antidegradants, pigments, and processing oils.

25       The essence of the present invention also finds utility in, for example, other rubber articles bonded to brass or brass-plated steel such as motor mounts, cutless bearings, springs, power belts, printing rolls,

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metal wire reinforced or braided hose, and wherever it is desired to secure rubber to metal or provide a flexible and strong, thermally stable bond between same.

The rubber articles of this invention can be produced by following a procedure which comprises: 1) preparing a rubber composition which contains at least one adhesion promoter of this invention, 2) surrounding the metal reinforcement with the rubber to conform to the desired shape of the rubber article being produced, and 3) curing (vulcanizing) the rubber article.

Vulcanization of the blends may be carried out in a press, an oven, or other suitable means until cross-linking has occurred to a satisfactory state of cure.

Thus, the standard techniques well-known to those skilled in the art for manufacturing rubber articles with metal reinforcing elements embedded therein can be employed in this invention. In other words, metal reinforcements can be incorporated into the rubber articles of this invention using the same techniques that are employed in incorporating metal reinforcements into ordinary rubber articles. Generally, reinforcing elements are simply surrounded by uncured rubber containing an adhesion promoter of this invention in a mold and vulcanized to produce the desired rubber article which has the metal reinforcement embedded therein.

In the practice of this invention generally from about 0.05 to about 20 parts per hundred parts of rubber

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by weight (phr) of the adhesion promoter will be employed in the rubber composition. It is generally preferred for 0.1 to 10 parts of adhesion promoter to be employed in the rubber composition per hundred parts of rubber by weight. It is more preferred for 0.5 to 6 phr of an adhesion promoter to be employed in the rubber composition. It should be noted that various blends of different adhesion promoters can be employed in the rubber compositions of this invention.

10 The adhesion promoters described herein can be distributed (mixed) throughout a rubber using any convenient, technique known to those skilled in the art. The rubber compositions of this invention are also cured using standard techniques well known to those skilled in the art. Generally, such rubber compositions are cured (vulcanized) under pressure at a temperature ranging from about 100°C to about 233°C with a metal reinforcement being embedded in the rubber composition so as to form a composite article. It is generally preferred for such composite articles to be cured at a temperature ranging from 100°C to 205°C.

The practice of the present invention has been observed to result in improved aged rubber-metal adhesion, in many cases with improved initial (original) adhesion. The following examples are included to further illustrate the rubber-metal composites within the scope of this invention and to compare them with other rubber-metal composites outside of its scope.

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Such comparisons clearly show the superior adhesion retention obtained by practicing the present invention. The following examples are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, all parts and percentages are given by weight.

#### SYNTHESIS METHODS FOR EXAMPLES 1-33

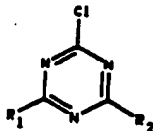
The substituted pyrimidines and triazines of the invention may be synthesized by a suitable synthesis route. The following synthesis Examples 1-25, Tables I, II, and III were made using the general procedure described by Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen, Journal of the American Chemical Society 73 2981 (1951). Tables I, II and III segregate the compounds according to convenient structural classification consistent with the foregoing publication and give the base used and crystallization method as well as physical properties and HPLC data. Synthesis Examples 27-33 shown in Table IV were made according to the general procedure described in Schaefer, Thurston, and Dudley, Journal of the American Chemical Society 73, 2990 (1951).

#### SYNTHESIS EXAMPLES

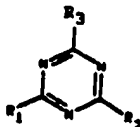
The general procedure described by Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen, Journal of the American Chemical Society 73 2981 (1951) was used to prepare the examples in Table I, II, III

TABLE I

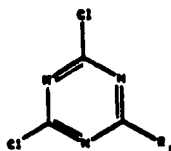
## SUBSTITUTED DIAMINO CHLOROTRIAZINES



Example	R1	R2	Base	Crystallized From	M.P. °C	Area Percent HPLC Analysis
1	Cyclohexyl-amino	Cyclohexyl-amino	NaOH	Acetone/Water	226-8	91.6
2	1-Methoxy-2-propylamino	1-methoxy-2-propylamino	NaOH	Acetone/Water	71-3	98.0
3	1,1-dimethyl-ethylamino	dicyclohexylamino	t-butyl-amine	Hexane	141-3	98.4
4	amino	amino	NH <sub>3</sub>	Acetone	Infusible	98.7
5	1,1,3,3-tetra-methylbutyl	1,1,3,3-tetra-methylbutyl	t-octyl-amine	Acetone	165-7	98.4
6	1,1-dimethyl-ethylamino	1,1-dimethyl-ethylamino	t-butyl-amine	Acetone	190-1	98.2
7	2-methyl-1-propanolamino	2-methyl-1-propanolamino	2-Amino-2-methyl-1-propanol	Toluene	173-5	98.2
8	anilino	anilino	NaOH	Acetonitrile water	195-197	91.9
9	4-dodecyl-anilino	4-dodecyl-anilino	NaOH	-	Oil	94.6
10	p-toluidino	p-toluidino	NaOH	Toluene	191-194	92.6
11	4-chloro-anilino	4-chloro-anilino	NaOH	Toluene	227-230	92.4
12	p-phenetidino	phenetidino	NaOH	Isopropanol	190-192	95.3
13	4-butyl-anilino	4-butyl-anilino	NaOH	Isopropanol	153-155	95.8
14	p-anisidino	p-anisidino	NaOH	Isopropanol	202-204	97.2

SUBSTITUTED TRIAMINOTRIAZINESTABLE II

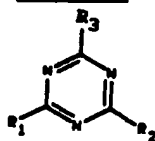
Example	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Base	Crystallised From	MP °C	Area Percent HPLC Analysis
15	anilino	anilino	anilino	NaOH	Isopropanol	229-230	99.7
16	4-butyl-anilino	4-butyl-anilino	4-butyl-anilino	NaOH	Isopropanol	210-213	97.3
17	4-dodecyl anilino	4-dodecyl anilino	4-dodecyl anilino	NaOH	-	oil	92.7
18	p-toluidino	p-toluidino	p-toluidino	NaOH	Toluene	220-222	93.7
19	4-chloro-anilino	4-chloro-anilino	4-chloro-anilino	NaOH	Toluene	254-256	98.4
20	4-hydroxy-anilino	4-hydroxy-anilino	4-hydroxy-anilino	p-amino-phenol	Toluene	>300	98.6
21	N-methyl-N-phenylamino	N-methyl-N-phenylamino	N-methyl-N-phenylamino	N-methyl-aniline	Isopropanol	117-119	99.1
22	p-anisidino	p-anisidino	p-anisidino	NaOH	Isopropanol	173-175	96.9
23	p-phenetidino	p-phenetidino	p-phenetidino	NaOH	Isopropanol	187-189	90.6
24	N-phenyl-p-phenylene diamino	N-phenyl-p-phenylene diamino	N-phenyl-p-phenylene diamino	NaOH	Isopropanol	212-215	88.4

SUBSTITUTED AMINODICHLOROTRIAZINETABLE III

Example	R <sub>1</sub>	Base	Crystallised From	MP° C	Area Percent HPLC Analysis
25	anilino	NaOH	Hexane /Toluene	131-133	90.3

ARYLOXY-S-TRIAZINES

The general procedure described by Schaefer, Thurston, and Dudley, Journal of the American Chemical Society 73, 2990 (1951) was used to prepare the examples in Table IV.

TABLE IV

Reaction of cyanuric chloride with Sodium Aryloxides in aqueous systems.

Example	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Crystallized From	M.P °C	Ar <sub>3</sub> Percent HF <sub>3</sub> Analysis
27	4-chloro- phenoxy	4-chloro- phenoxy	4-chloro- phenoxy	Acetone	213-215	93.3
28	Cl	4-tert-octyl phenoxy	4-tert-octyl phenoxy	THF/water	104-106	96.2
29	Cl	phenoxy	phenoxy	Hexane	117-119	92.7
30	Cl	4-dodecyl phenoxy	4-dodecyl phenoxy		oil	89.7
31	4-formyl phenoxy	4-formyl phenoxy	4-formyl phenoxy	Toluene	164-168	92.6
32	Cl	4-tert-butyl phenoxy	4-tert-butyl phenoxy	Isopropanol	108-110	91.2
33	phenoxy	phenoxy	phenoxy	Methanol	233-234	—



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Example 262,4,6-Tris(N,N-dicyclohexylamino)1,3,5-triazine

In a one liter, three-necked, round-bottom flask equipped with a thermometer, a condenser, and a mechanical stirrer, was placed 366 grams (2 moles) of 99 percent dicyclohexylamine. Finely ground 99 percent cyanuric chloride (.1 mole, 18.6 parts ) was added with good stirring. Over a period of six hours the reaction mixture was heated to 250°C., and held for an additional hour at 250°C. The reaction was followed by high performance liquid chromatography by observing the disappearance of the starting-cyanuric chloride, and the conversion of the intermediate dichloro, and mono chlorotriazines to the tri-substituted compound. The reaction mixture temperature was adjusted to 60°C., and 300 ml of toluene was added. The title compound precipitated, and was isolated by filtration. The filter cake was washed with hot water to remove dicyclohexylamine hydrochloride. The m.p. was 325-327°C. The yield was 79.3 percent. The infrared spectrum was consistent with the structure. Relative area HPLC analysis of the product showed it to be 97.9 percent pure.

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ADHESION PROMOTER UTILITY EXAMPLES- [Table A]

All of the examples of Table A utilize a masterbatch of the following recipe.

	Parts by Weight
5 Natural Rubber (SMR 5CV)	100.0
Carbon Black	58.0
Zinc Oxide	7.0
Stearic Acid	2.0
10 Naphthenic Oil	6.0
Antiozonant N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylene-diamine	2.0
Total	175.0

- 15 The Masterbatch is prepared by mixing the rubber in an internal mixer and after one minute adding the zinc oxide and one-half of the carbon black. After three minutes, the balance of the ingredients is added. The unit is "swept-down" at five minutes and the material
- 20 discharged at seven minutes at from about 122°C to about 150°C.

Two such batches as described above are prepared and milled together to realize the final Masterbatch.

- Employing the ingredients indicated in Test Recipe below
- 25 (which are listed in parts per hundred of rubber by weight), several rubber compositions were compounded in the following manner:

- one half of the Masterbatch, bonding agent, adhesion promoter, accelerator, sulfur and balance of the Master-
- 30 batch are added sequentially to an internal mixer and subsequently discharged at 100°C. Each example is then mill blended for five minutes.

TEST RECIPE

	Masterbatch	175.00
35	Adhesion Promoter(variable)	2.00
	Accelerator **	0.70
	Sulfur (80% oiled sulfur)	6.25
		183.95

\*\*N,N'-dicyclohexyl-2-benzothiazylsulfenamide

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Test samples of each of the composition examples, which are similar to commercial tire breaker compositions were molded and cured at 160°C according to specifications given in ASTM D-1871 for a time equal to  
5 the  $T_c$ 90 plus 2 minutes.

The cured samples were oven aged for two days at 121°C and three days in steam at 121°C. Wire Adhesion Tests were then conducted according to modified ASTM D-2229, "Adhesion To Steel Cord" with Newtons to  
10 pull-out measured at 121°C. The adhesion pads were cured for 40 minutes at 160°C. using 2x2 brass coated steel wire.

The modification of ASTM D-2229 consisted of using specifically a Chatillon movable stage and digital force  
15 gauge. The bottom grip holds the block of rubber firmly in place. The top grip holds the wire firmly in place. The bottom grip is mounted to a stage that lowers itself, exerting tension between the ripped wire and the block in which it is embedded. The digital force gauge  
20 attached to the top grip that holds the wire measures the force necessary to pull the wire from the block in which it is embedded.

The wire adhesion data for each example shows the force in Newtons necessary to pull or remove the brass  
25 coated steel reinforcing wire from a 25.4 mm embedment in the vulcanized pad at a rate of 50.8 mm/minute. This "pull-out" force is followed (in the aged samples) by the percentage of original force retained. Finally, the amount of rubber remaining on the wire was determined by

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visual examination and has been reported as percent retained rubber coverage, wherein 5 represents 100% coverage; 2 represents 40% coverage; etc.

The rubber coverage measurement is significant in that it visually represents the adhesion of the rubber composition to the brass plated steel cord. As is well known to those skilled in the art, the amount of rubber adhering to the steel cord after it has been pulled from a cured adhesion pad represents the relationship of the adhesive force attaching the rubber composition to the surface of the steel cord and the tear strength of the rubber composition itself. Large percentages of rubber coverage indicate that the adhesion to the steel cord exceeds the internal strength of the rubber composition itself, i.e., tear strength. Therefore, when the rubber coverage is very high it can be concluded that the metal to rubber adhesion is greater than the force measured to pull the steel cord out of the rubber pad since the force measured was a result of the rubber composition rupturing and not the metal to rubber interface.

Normal or unaged testing is merely a measurement of the initial adhesion properties between the rubber composition and the metallic reinforcement. High temperature aging is an accelerated test and is significant in determining the chemical stability of the chemical bonds formed between the rubber composition and the metallic reinforcement when exposed to heat in service.

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**TABLE A****WIRE ADHESION TESTING**

		<u>AGED 2 DAYS AT 121°C.</u>				
		<u>UNAGED</u>	<u>WIRE</u> <u>COVERAGE</u>	<u>AGED</u>	<u>%</u> <u>RETENTION</u>	<u>WIRE</u> <u>COVERAGE</u>
5	EX. 1	407.3	5.0	395.2	97.0	4.5
10	EX. 2	433.8	4.0	377.1	86.9	4.5
	EX. 3	446.0	4.5	378.0	84.8	3.0
	EX. 4	502.0	4.5	364.8	72.7	3.5
	EX. 5	389.1	5.0	371.1*	95.4	4.3
	EX. 6	460.5	5.0	371.4	80.7	3.5
15	EX. 7	459.6	4.5	398.6	86.7	4.5
	EX. 8	460.0	5.0	391.3	85.1	5.0
	EX. 9	448.9	4.5	402.5	89.7	4.3
	EX. 10	470.7	4.8	399.6	84.9	4.3
	EX. 11	416.9	4.5	401.8	96.4	4.3
20	EX. 12	425.8	4.5	432.1	101.5	4.0
	EX. 13	438.7	4.3	374.4	85.3	4.0
	EX. 14	471.6	5.0	305.3*	64.7	3.5
	EX. 15	439.9	4.0	362.3	82.4	5.0
	EX. 16	383.6	4.8	367.3	95.8	4.0
25	EX. 17	415.6	4.5	329.1	79.2	4.5
	EX. 18	392.0	4.5	382.3	97.5	4.5
	EX. 19	358.7	4.5	381.4	106.3	4.0
	EX. 21	412.5	3.5	361.9*	87.7	3.0
	EX. 22	418.1	4.5	182.5*	43.6	3.0
30	EX. 24	436.2	5.0	346.5	79.4	5.0
	EX. 25	443.5	5.0	418.7	94.4	4.5
	EX. 26	398.7	4.5	376.2	94.4	3.5
	EX. 27	420.0	5.0	430.3*	102.5	4.5
	EX. 28	472.9	5.0	395.1*	83.5	4.5
35	EX. 29	447.8	5.0	447.8	100.0	4.5
	EX. 30	433.4	4.5	433.4	100.0	4.5
	EX. 31	409.8	4.3	409.8	100.0	4.5
	EX. 32	494.7	5.0	354.4*	71.6	4.5
	EX. 33	449.4	5.0	364.0	81.0	4.0

40

\* STEAM AGED 3 DAYS AT 121°C.

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Table A presents the results of certain of the preferred compounds of Structure (I) in the 100% natural rubber masterbatch. Examples 1-31 show that the compounds of the invention show excellent unaged  
5   adhesion. After oven or steam aging, the compounds of the invention show excellent properties for % retention of adhesion and wire coverage.

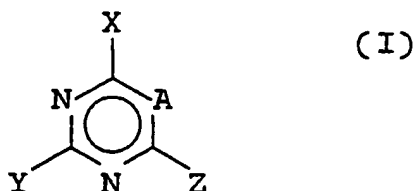
In conclusion, it is to be understood that the methods and rubber compounds disclosed herein are  
10   exemplary only. The subject invention is not to be limited by the examples set forth herein. As will be apparent to those skilled in the art, the formulation of the rubber composition can be varied within the scope of the whole specification disclosure by selection or  
15   deletion of various rubbers and ingredients of the types set forth herein as well as the amounts thereof without departing from the spirit of the invention herein disclosed and described. The scope of the invention shall be understood to be described and limited only by  
20   the attached claims.

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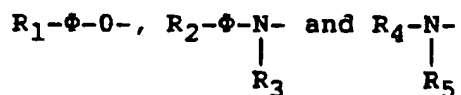
What is claimed is:

1. A reinforced elastomeric composition produced by curing a blend comprising:

- a) vulcanizable rubber;
- 5       b) brass coated metal reinforcement;
- c) sulfur or sulfur donor; and
- d) a compound represented by Structure (I)



wherein A is N or C-H and X, Y and Z are independently selected from the group consisting of chloro,



wherein  $R_1$  may be hydrogen, chloro, acyl, or  $C_1-C_{12}$  alkyl;

$R_2$  may be hydrogen,  $C_1-C_{12}$  alkyl, chloro, hydroxy, alkoxy, or anilino;

$R_3$  may be hydrogen,  $C_1-C_4$  alkyl or phenyl;

$R_4$  may be hydrogen,  $C_1-C_8$  alkyl, cyclohexyl,  $C_1-C_{12}$  hydroxyalkyl, or  $C_1-C_{12}$  alkoxyalkyl;

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R<sub>5</sub> may be hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, cyclohexyl, or C<sub>1</sub>-C<sub>12</sub> hydroxyalkyl; with the proviso that Z may not be chloro when both X and Y are chloro and R<sub>2</sub> may not be anilino when X, Y or Z is chloro.

5        2. The reinforced elastomeric composition of claim 1 wherein said blend further comprises a sulfur cure accelerator.

3. A reinforced elastomeric composition according to claim 2 wherein said blend is further characterized  
10    by:

- a) from about 0.05 to about 20 parts of a said compound represented by Structure (I);
- b) from about 0.2 to about 10.0 parts of said sulfur per 100 parts by weight of rubber;  
15    and
- c) from about 0.1 to about 5.0 parts of said sulfur cure accelerator per 100 parts by weight rubber being present therein.

4. A reinforced elastomeric composition according  
20    to claim 3 wherein said blend further comprises from about 0.05 to about 20 parts of at least one bonding agent selected from the group consisting of cobalt salts, 2,3,5,6-tetrachloro-1,4-benzoquinone, a resorcinol/ formaldehyde donor and a resorcinol  
25    derivative.

5. The reinforced elastomeric composition of claim 2 wherein the sulfur cure accelerator is a benzothiazole sulfenamide, 2-mercaptobenzothiazole or benzothiazyl disulfide.



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6. The reinforced, elastomeric composition of  
 claim 4 wherein the bonding agent is a resorcinol  
 5 derivative.

7. The reinforced, elastomeric composition of  
 5 claim 1 wherein the vulcanizable rubber is selected from  
 the group consisting of natural rubber, synthetic  
 rubber, and blends thereof.

8. The reinforced, elastomeric composition of  
 claim 1 wherein the compound of Structure (I) is further  
 10 defined in that A is N, X, Y and Z are the same and are  

$$\begin{array}{c} R_2-\phi-N- \\ | \\ R_3 \end{array}$$

15 9. The reinforced, elastomeric composition of  
 claim 1 wherein the compound of Structure (I) is further  
 defined in that A is N, X is Cl, Z and Y are  $R_2-\phi-N-$   

$$\begin{array}{c} | \\ R_3 \end{array}$$
  
 20

10. The reinforced, elastomeric composition of  
 claim 9 wherein said compound of Structure (I) is  
 further defined in that  $R_2$  and  $R_3$  are hydrogen.

11. The reinforced, elastomeric composition of  
 25 claim 8 wherein said compound of Structure (I) is  
 further defined in that  $R_2$  and  $R_3$  are hydrogen,  $C_1-C_{12}$   
 alkyl, anilino.

12. A process for producing a reinforced  
 elastomeric composition comprising the steps of:

30 A) preparing a blend comprising:  
 a) vulcanizable rubber;

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Attorney  
Office:

5

- b) brass coated metal reinforcement;
  - c) from about 0.05 to about 20 parts of a compound of Structure (I);
  - d) from about 0.2 to about 10.0 parts of sulfur per 100 parts by weight of rubber;
  - e) from about 0.1 to about 5.0 parts of sulfur cure accelerator per 100 parts by weight rubber; and
- B) subjecting said blend to curing conditions.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/04690

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K5/3492; C08K5/3462; C08L21/00; C08J5/10		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	RESEARCH DISCLOSURE vol. 157, no. 5, May 1977, HAVANT GB pages 58 - 59 DISCLOSED ANONYMOUSLY 'Rubber/copper bonding by the use of triazine compounds' see nr 15778, whole article -----	1-7, 12
X	US,A,4 339 359 (R.S.BEZWADA) 13 July 1982 see claim 1 -----	1-5, 12
<p><sup>10</sup> Special categories of cited documents : <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
05 AUGUST 1993	18.08.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	VAN HUMBEECK F.	

US 9304690  
SA 74466

05/08/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4339359	13-07-82	None	

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